

Aqueous coating compositions based on room-temperature crosslinking latex

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Inventor:

HIRSH MARC STEPHEN (US); LEE SHARON (US);

SAY TERENCE E (US); ZESZOTARSKI JONATHAN C

(US)

Applicant:

RHONE POULENC SPEC CHIM (US)

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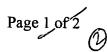
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Abstract of EP0653469

The aqueous coating composition according to the invention is based on latex of a polymer derived from the polymerisation of the following monomers: (a) acetoacetoxyethyl acrylate or acetoacetoxyethyl methacrylate; (b) glycidyl acrylate or glycidyl methacrylate; (c) one or a number of polymerisable acids containing ethylenic unsaturation and (d) one or more monomers copolymerisable with the above; in which the total percentage by weight of (a), (b) and (c) in the polymer latex composition is between approximately 2 % by weight and approximately 60 % by weight relative to the total quantity of solids contained in the latex and in which the total percentage by weight of (d) in the composition of the latex is between approximately 97 % by weight and approximately 40 % by weight relative to the total quantity of polymer solids contained in the latex. The aqueous compositions according to the invention can be employed especially in glues, pressure-sensitive adhesive compositions, industrial paints, decorative paints and coatings for wood.

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Aqueous coating based compositions one room-temperature crosslinking latex

Claims of **EP0653469**

- 1. Aqueous composition of coating containing polymeric latex, characterized in that the polymer derives from the following monomers:
- (A) acétoacétoxyéthyl acrylate or acétoacétoxyéthyl methacrylate;
- (b) glycidyl acrylate or glycidyl methacrylate;
- (c) one or more polymerizable acids with ethylene non-saturation and
- (d) one or more monomers copolymÃ@risables with the precedents; and in which the total percentage in weight of (A), (b) and (c) in the polymeric composition is included/understood between approximately 2 % in weight and approximately 60% in weight compared to

the total quantity of solids contained in the aqueous emulsion and in which the total percentage in weight of (d) in the polymeric composition is included/understood between approximately 97 % in weight and approximately 40 % in weight compared to the total quantity of polymeric solids contained in the aqueous emulsion.

aqueous 2.Composition of coating according to claim 1, characterized in that the aforementioned latex has a pH ranging between approximately 6,5 and approximately 10.

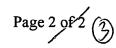
- 3. Aqueous composition of coating according to claim 1, characterized in that the monomer (c) drift of an acid monomer at acrylic base.
- 4. Aqueous composition of coating according to claim 3, characterized in that the monomer (c) is selected in the group including/understanding the acrylic acid, the methacrylic acid and their mixtures.
- 5. Aqueous composition of coating according to claim 1, characterized in that at least one of the monomers (d) drift of an acrylic ester.

aqueous 6. Composition of coating according to claim 5, characterized in that at least one of the monomers (d) comprises a alkyl acrylate or a alkyl methacrylate in which the group alkyl contains between approximately 1 and approximately 8 atoms of carbon.

- 7. Aqueous composition of coating according to claim 6, characterized in that at least one of the monomers (d) is selected in the group including/understanding the ethyl acrylate, methyl methacrylate, the acrylate of butyl and their mixtures.
- 8. Aqueous composition of coating according to claim 1, characterized in that at least one of the monomers (d) drift of aromatic or aliphatic monomers vinyl.
- 9. Aqueous composition of coating according to claim 8, characterized in that at least one of the monomers (d) contains of styrene.

aqueous 10. Composition of coating according to any of claims 1 to 9, characterized in that up to 80 % in weight, preferably jussqu' to 50 % in weight of the aforesaid latex is replaced by another binder chosen among the latexes acrylate, styrÃ@ne/acrylate and copolymers acetates, the dispersion aqueous of polyurethane, polyester, epoxy, alkydes such resins polyurethanes, epoxy and alkydes.

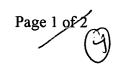
- 11 Aqueous composition of coating according to claim 1, characterized in that:
- (A) includes/understands the acA@toacA@toxyA@thyl methacrylate;
- (b) includes/understands the glycidyl methacrylate;
- (c) includes/understands a mixture of acrylic acid and acid methacylic;
- (d) includes/understands a mixture of ethyleneglycol diméthacrylate, styrene, acrylate of butyl, methacrylate of ethyl methyl and acrylate.



aqueous 12. Composition of coating according to claim 2, characterized in that the pH of the aforesaid latex is adjusted using a water-soluble base selected in the group comprising ammonia, sodium hydroxide, a quaternary ammonium hydroxide and their mixtures.

- 13 Aqueous composition of coating according to revenaication 12, characterized in that the aforementioned base includes/understands the hydroxide of tA©tramA®thylammonium.
- 14 Aqueous composition of coating according to claim 1, characterized in that the aforementioned composition includes/understands one or more additives chosen in the comprising group of thickeners, antifoaming, agents modifying, agents of coalescence, dispersants, pigments, dyes, surfactant, surfaceactive, anti-blockants agents and their mixtures.
- 15.Procédé of surface coating comprising the stage of the application of one painting to water containing a composition containing polymeric latex as defined in the unspecified one of claims 1 to 14.
- 16 Pocédé according to claim 15 in which the reticulation is done at temperatures ranging between approximately 5 Degree c and approximately 40 Degree c.
- 17 Process according to the claim 16 in which the aforementioned reticulation requires from 12 to approximately 48 hours.
- 18 Proceeded according to claim 17, characterized in that treated surface is selected in the group including/understanding the partitions dry, wood, the skirtings, metal, the concrete, surfaces out of plastics and glass.
- 19 Composition of painting to water including/understanding an aqueous composition containing polymeric latex as defined in the unspecified one of claims 1 to 14.
- 20 Use of an aqueous composition of coating as defined in the unspecified one of claims 1 to 14 to prepare adhesives, adhesives sensitive to the pressure, varnishes of overprintings of compositions of industrial painting.

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Description of EP0653469 Technical field of the invention The present invention belongs to the field of the aqueous compositions of coating, used for example like paintings with water and which reticulate at the ambient temperature and high temperatures. The compositions of coating which reticulate under the environmental conditions are known for a long time. The oldest compositions of this type are the coatings based on siccative oils which reticulate by oxidation with the air. The other compositions of coating developped at the point more recently are the compositions which rest on the reactions between epoxy and the carboxylic acid, isocyanate and moisture, the polyaziridine and the carboxylic acid, activated methylene and the unsaturated acrylic acid. Patent the USA 3 554 987 described of film forming copolymers of the acrylic acid, the acétoacétoxyéthylméthacrylate and the monomers with which they are copolymérisés. According to patent the USA 4 408 018 one mixes polymers comprising of the hanging groupings acétoacétate with polyacrylates comprising more than one acrylic grouping unsaturated and one reticulates them by addition of Michael by using a strong base like catalyst. The European patent application EP-A 227 454 also described a reticulation obtained by addition of Michael. In this patent application, one mixes compounds containing a great number of free acétoacétate groups with compounds containing a great number of acrylic groups with ethylene nonsaturation and one reticulates them by addition of a strong base or an organometallic compound. The patent South-African N DEG 85-2044 described of the compositions of coating which reticulate at the ambient temperatures and which are obtained starting from a composition containing a great number of activated methylene groups and carbonyl groups with ethylene non-saturation. In the article of A. Noomen, entitled "Curable Ambient Temperature" Coatings Based one Two-Pack Binders", Organic Coatings Conference, Athens, Greece, June 1987,

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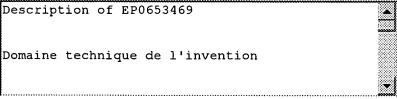
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the discussion relates to compositions of coating which reticulate within the framework of a reaction of addition of Michael between acétoacétate-ketimine groups and acrylic resin-malonate groups. In patents the USA 3 305 601 and the USA 4 028 294 and it European patent application EP-A 226 171, one describes compositions of thermohardening coatings which rest on the reaction between epoxy and the carboxylic acid. Patent the USA 4 906 684 door on polymeric compositions which reticulate at the ambient temperature and which contains acétoacétoéthyl-(méth)acrylate, glycidyl-(méth) acrylate, a polymerizable acid and a monomer copolymérisable. Applied like coating to a substrate. the aforementioned coating reticulates and hardens at the ambient temperatures. These compositions are sold by Rhône-Poulenc Inc under the mark: RESIN AMBICURE TM. Being given the request increasingly more important for coating decorative and protective being able to support a great number of applications and to resist all kinds of conditions imposed by the environment, there is permanently a need for new compositions.

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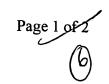
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In English:

Disclosed invention The present invention relates to aqueous compositions of coating containing latexes (polymeric in dispersion in water) which reticulate at the ambient temperature and high temperatures. On a side, the present invention belongs to the field of the compositions of coating which contain a acétoacétoxy group, a glycidyle group and a carboxylic acid group. On another side, the present invention is connected with the film forming acrylic polymers which comprise free acétoacétoxy groups, glycidyle groups and groups acid carboxylic. The aqueous compositions of coating according to the present invention are based on a polymeric latex which contains (A) of the acétoacétoxyacrylate of ethyl or methacrylate, (b) of the glycidylacrylate or methacrylate, (c) a polymerizable acid with ethylene non-saturation and (d) a monomer which can copolymériser with the preceding monomers, and in which the total percentage in weight of (A), (b) and (c) contained in polymer is included/understood between at least approximately 2 % and to most approximately 60 % in weights of the total quantity of solid polymers contained in latex in which (d) is present at a rate of approximately 40 at approximately 97 % in weight compared to the total quantity of solid polymers contained in the latex and in which the pH of dispersion is between approximately approximately 10. Applied to a substrate, the aqueous composition of coating reticulates at the ambient temperature until thermodurcissement complete. One uses this aqueous composition of coating as binder, preferably, in particular, in paintings with water. Description of the preferential modes of realization The component (A), the ethyl acétoacétoxyacrylate or methacrylate monomers implemented according to the present invention, can be obtained by reaction between dicetene and the hydroxyacrylate of ethyl or methacrylate. The acétoacétoxyéthyle group comprises a methylene group located between two carbonyls and it is because of this position which one

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says that it acts of "active" a methylene group. Thanks to their double connections, these groups are capable of addition of Michael and can react with the epoxy groups. In the preferential mode of realization, the quantity of this component present in the aqueous discrepancy varies between approximately 0,5 and approximately 20 % in weight. The component (b), namely the glycidylacrylate or methacrylate monomers, implemented according to the present invention are well-known monomers which one finds in the trade. These monomers can be obtained by esterification of the acrylic or methacrylic acid with the glycidol or the épichlorohydrine, followed of a deshydrohalogenation. The glycidyle group is able to react with groups methylene credits, groups acid carboxylic and other epoxy groups. In the preferential mode of realization, the quantity of this component present in the aqueous discrepancy varies between approximately 1,0 and approximately 15,0 % in weight.

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Exposé de l'invention

La présente invention concerne des
compositions aqueuses de revêtement à base de
latex (polymère en dispersion dans l'eau) qui

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In English:

The component (c) includes/understands polymerizable acid monomers which are mono or polycarboxylic acids well-known comprising a polymerizable connection by molecule. These acids comprise in general of 3 with approximately 24 atoms from carboxylic carbon and 1 or 2 groups acid per molecule. As examples of these acids one can quote the acids acrylic resin, methacrylic, maleic, fumaric, itaconic, ethacrylic, crotonic, citraconic and semiesters of the acids dicarboxylic in which esterified the alcohol group contains of 1 with approximately 20 carbon atoms. As examples of suitable semi-esters the méthylhydrogénofumarate will be quoted, the benzylhydrogénomaléate, the butylhydrogénomaléate, the octylhydrogéno-itaconate, the dodécylhydrogéno-citraconate and others similaires. Les acid preferential that one implements according to the present invention are the acids acrylic resin and methacrylic. In the preferential mode of realization, the quantity of this component present in the aqueous discrepancy varies between approximately 0,5 and approximately 3,0 % in weight. The component (d) includes/understands monomers copolymérisables which, according to the present invention, can jointly be implemented with the three other families of monomers indicated above. It acts of any of these well-known monomers which comprise only one polymerizable group with ethylene nonsaturation by molecule and which can be copolymérisés with the other monomers. The quantity of this component contained in dispersion varies between approximately 40 and approximately 97 % compared to solid polymers, the preferential quantity lying more particularly between approximately 60 and approximately 90 % in weight. Any monomer in measurement of copolymériser with the components (A), (b) and (c) can be implemented according to present the invention. Il acts of the monomers which do not comprise likely groups, under the conditions of polymerization, to react with the acétoacétoxy groups, glycidyle or acid carboxylic. The types and

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the quantities of monomers copolymérisables implemented according to the present invention vary according to the particular final application for which the product according to the present invention is intended. These variations are well-known and can be easily determined by the specialist of the profession. The comonomères implemented preferably according to the present invention are the methacrylate and acrylate esters in which the ester group is an alkyl group containing from 1 to 8 carbon atoms. As examples of such monomers one can quote the acrylic and methacrylic esters in which the ester group contains of 1 with approximately 20 carbon atoms, such as, for example, the methyl acrylate, the methyl methacrylate, the ethyl acrylate, the ethyl methacrylate, the propyl acrylate, the acrylate of butyl, the methacrylate of 2-éthylhexyle. the acrylate of décyle, the methacrylate of lauryle, the benzylacrylate and other similar. The other acrylic or methacrylic esters which can be implemented according to the present invention are multipurpose acrylates or methacrylates, such as, for example, the ethyleneglycol diméthacrylate, the hexanediol diacrylate, etc. These esters can be implemented in quantities being able to go until approximately 5 % in weight compared to the total weight of the monomers. The other monomers copolymérisables are the vinyl aromatic monomers, such as styrene, the vinyltoluene, alpha-méthylstyrène and other similar as well as nitriles, such as, for example, acrylonitrile and the acrylamide. The additional monomers copolymérisables that one can implement according to the present invention are the derivatives of hypothetical vinyl alcohol, for example, the vinyl esters aliphatic, such as vinyl formate, the acetate of vinyl, the vinyl propionate, the vinyl butyrate, the vinyl ester of the acid versatic and other similar. The compositions according to the present invention are obtained by polymerization of monomers emulsified in water according to processes' of polymerization in alkaline emulsion. These processes can be done uninterrupted, by batches, stages or into discontinuous. The surface-active ones implemented to emulsify the monomers are surface-active anion the and non-ionic ones like their mixtures. As examples of surface-active anion being able to be used one can quote the organosulfates and sulphonates, for example, alkyl, aryl and alkaryl sulphates and potassium and sodium sulphonates. such as sodium 2-éthylhexyl-sulphate, potassium 2-

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éthylhexyl-sulphate, the sodium nonylsulfate, the sodium laurylsulfate, the potassium méthylbenzènesulfonate, the potassium toluènesulfonate and the sodium xylènesulfonate; fatty alcohols higher, for example, stearyl, lauryle. etc, éthoxylés and sulfonatés; the dialkyl esters of salts of the alkaline metal acid sulfosuccinic, such as the diamyl sulfosuccinate of sodium and the dioctyl sulfosuccinate of sodium; products of condensation of the sulphonic acid formaldehyde-naphthalene; salts of alkaline metals, salts partial of alkaline metals and free phosphate complex organic esters acids. As examples of surface-active non-ionic being able to be implemented according to the present invention one can quote polyethers, such as the condensates of oxides of ethylene and propylene which include/understand ethers and thioethers of alkyl and of alkaryl polyethyleneglycol and polypropyleneglycol with linear or ramified chains; alkylphénoxypoly (éthylèneoxy)-ethanols comprising of the alkyl groups containing from approximately 7 with approximately 18 carbon atoms and comprising approximately 4 with approximately 240 reasons éthylèneoxy, such as the heptylphénoxy-poly(éthylèneoxy)éthanols, the nonylphénoxy-poly(éthylèneoxy)éthanols; the derivatives polyoxy-alkylene of the hexitol (including the sorbitans, sorbides, mannitans and mannides); esters of partial fatty acids with long chains, such as the derivatives polyoxyalkylene of sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostéarate, sorbitan tristéarate, sorbitan monooléate and sorbitan trioléate; condensates of ethylene oxide with a hydrophobic base, the aforementioned base being obtained by condensation of propylene oxide with propylene glycol; the condensates containing of sulphide, for example, those obtained by condensation of ethylene oxide with higher alkyl mercaptans, such as the nonyl, dodécyl or tétradécyl mercaptans or with alkylthiophénols in lequels the alkyl group contains approximately 6 with approximately 15 carbon atoms; the derivatives oxidizes ethylene of carboxylic acids with long chains, such as the acids lauric, myristic, palmitic or oleic or the mixtures of acids such as the fatty acids of tall oil; and the derivatives oxidizes alcohol ethylene with long chains such as alcohols octylic, decylic, laurylic or cetyl. The quantities of surface-active implemented in the process of polymerization in emulsion vary between approximately 0,01 and approximately 10 % in

weight, preferably between approximately 0,2 and approximately 5 % in weight compared to the total weight of monomers and water. In more of surfaceactive, the system of polymerization in emulsion can also contain protective colloids. Like examples of protective colloids, one can quote protective colloids comprising of the bonds ether, such as the hydroxyméthylcellulose, the hydroxyethylcellulose, the éthyl-hydroxyethylcellulose, carboxymethyl cellulose, the éthoxylés derivatives of the starch and other similar. Other colloidal substances of protection can be used also, only or in partnership with products comprising of the connections éther D' other colloids of protection comprise polyvinyl alcohols hydrolized partly or entirely, polyacrylic acid, polyacrylates of sodium and other metals alkaline, polyacrylamide, maleic poly(méthyl vinyl éther/anhydride), polyvinylpyrrolidone, starches water-soluble, watersoluble adhesive, gelatine, alginates, such as alginates sodium or potassium, casein, agar and gums natural and synthetic, such as the guar, the xanthane, the gum arabic and the gum tragacanthe. The colloids of protection can be implemented in quantities ranging between approximately 0,1 % in weight and approximately 2 % in weight compared to the total weight of the polymer dispersion. Within the framework of this invention, one can perfectly plan to use the other surface-active ones. The monomers implemented in the present invention are polymerized preferably using a traditional initiator of polymerization to free radicals or a system of initiators (whom one can also call catalyst of polymerization by addition, catalyst of vinyl or initiating polymerization of polymerization). preferably, but not necessarily, very soluble in the eau. Parmi the aforementioned initiators, one counts the hydrogen peroxides, the hydroperoxide of butyl tertiary sector, the hydroperoxide of cumene, persulphates, perphosphates and perborates of alkaline metals (such as, for example, sodium, potassium or lithium) or of ammonia; the nitriles azo, such as alpha, alphaazobisisobutyronitrile, and the systems redox comprising of the combinations such as the mixtures of hydrogen peroxide, t-butyl peroxide or other similar and of any of iron salts. titanous salts, formaldehyde sulfoxylate of zinc or formaldehyde sulfoxylate of sodium; persulphate, perborate or perchlorate of alkaline metals or ammonium in partnership with an alkaline metal bisulfite, such as the sodium métabisulfite; and the

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alkaline metal persulphate in partnership with an acid arvlphosphinic, such as the phosphonic acid benzene and other similaires. La quantity of initiator of polymerization implemented will not be higher than that necessary to obtain a very complete conversion of the monomer at low prices. The quantity of initiator varies in general between approximately 0,1 and 1 % in weight compared to the weight of the added monomers. The emulsification and the reaction of polymerization can be carried out by any known process implemented to obtain polymers in emulsion. For example, the monomers, catalysts, surfaceactive, the possible colloids of protection and the possible agents for transfers of chains, such as the alkylmercaptans, can all be introduced into the engine, agitated in a suitable way in order to obtain an emulsification at a temperature ranging between approximately 30 Degree c and approximately 95 Degree c until polymerization is complete. One can also lead the reaction in the following way: one introduces water, the surface-active ones and the possible colloids of protection in the engine, one heats until the reactional temperature is reached and, then, one adds the monomers and a solution of initiator in the engine while agitating. There is still another method which consists in pre-emulsifying the monomers in a part of water and a part of surfaceactive with the initiator, to introduce the pre-emulsion into the engine which contains the remainder of water and the surface-active one.

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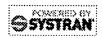
Le composant (c) comprend des monomères acides polymérisables qui sont des acides mono ou polycarboxyliques bien connus comportant une liaison polymérisable par molécule. Ces acides comportent en règle générale de 3 à environ 24 atomes de carbone

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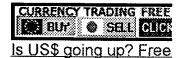
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In English:

To obtain compositions forming of the coatings having higher properties when they reticulate at the ambient temperature or high temperatures, is needed, in the preferential modes of realization, that the glycidyl and the acid is present in certain preferential reports/ratios. It was found that the acétoacétoxy group and groups it glycidyle must be present in a report/ratio in weight lower or equal to 0,5, the reports/ratios in weight being calculated compared to the weight of the acétoacétoxyéthyl (méth)acrylate and the glycidyl (méth)acrylate, the glycidyle group and the carboxylic acid group must be present in a report/ratio in weight higher than 1,0, the reports/ratios in weight being founded on the weight of the glycidyl (méth)acrylate and (of) acid the polymérisable(s) with non-saturation éthylénique.Par elsewhere, the percentage in total weight of the three monomers (component (A), (b) and (c) used to form polymer must be at least approximately 2 % and not to exceed approximately 60 %, the aforementioned percentages referring itself to the total weight of all the monomers implemented to form polymer. The quantity of water implemented to obtain the compositions according to the present invention is a function of the content of solids which one wishes to have in finished polymeric latex. In general, the content of solids is included/understood between approximately 20 % and approximately 70 % of weight. The content of solids lies preferably between approximately 40 % and approximately 60 % of weight. As soon as polymerization in emulsion is finished, one adjusts the pH with a value ranging between approximately 6,5 and approximately 10 with a water-soluble base. The bases which are appropriate are bases containing alkaline metals, of ammonia and quaternary ammonium. Like examples of adapted bases, one can quote ammonia, the hydroxides of sodium, potassium, tétraméthylammonium, tétraéthylammonium, tétrabutylammonium, benzyl-triméthylammonium and other similar. One of the preferred bases more

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particularly is the hydroxide of tétraméthylammonium. The aqueous composition of coating can contain, in more of latex noted above, any binder used in the compositions of coating of this type. As binder one can quote the latexes acrylate. Styréne/acrylate and copolymers acetate, aqueous polyurethane dispersions, of poyester, of epoxy, alkydes and the resins polyurethanes, epoxy and alkydes. These binders can replace up to 80 % in weight, preferably up to 50 % in weight, of latex present in the aqueous compositions of coating of this invention. Intended to be used as binder in paintings, the aqueous compositions of coating containing polymeric latex according to the present invention can be applied to a great number of substrates to form films and coatings which reticulate and give thermodurcies compositions to the ambient temperature or high temperatures. The preferential temperatures of reticulation vary between approximately -10 Degree c and approximately 100 DEG C One of the applications which are appropriate particularly for the products according to the invention lie in the coatings of the bois. On understands here by coatings of wood all the types of wood and all shapes of coatings of wood. such as pieces of furniture, floor coverings commercial, residential floor coverings, grounds of patios, industrially varnished parquet floors, skirting, frames, mouldings, storage units and other similar. When they are used as coatings of wood, aqueous dispersions according to the invention can comprise other additives intended to increase their performances. Like examples of these additives, one can quote thickeners, the antifoaming ones, and glycols intended to prevent the premature reticulations, the agents of coalescence, the pigments, the activators of bases. These additives represent usually less than 5 % in weight of the solids present in final aqueous dispersion. Used for the coatings of wood, the aqueous compositions according to the present invention, possibly containing additives, are applied quite simply to the surface wood, their thickness lying between approximately 25 driven m and approximately 75 driven m, using a brush, of a roller and any other average good known in the trade. Then, one lets dispersion reticulate at temperatures varying between approximately 5 Degree c and approximately 40 Degree c, preferably, in particular, between approximately 5 Degree c and approximately 15 DEG C In the 12 hours which follow the application.

dispersion starts to reticulate and forms a hardened film. The operation of reticulation is finished to at least 85 % at the end of approximately 48 hours and gives a transparent, colourless film and brilliance. The aqueous compositions according to the invention are more particularly usable in paintings with the eau. De such paintings are applicable on any support such as a wall untreated, wood, facings, metal, concrete, plastics, glass and similar. Utisées in paintings, the final formulations can contain additives to improve the properties. Examples of such additives include thickeners, agents démoussants, modifiers of open time and glycols to avoid a premature reticulation, coalescent agents of the anti-blocking. the activators, catalysts, pigments and similar agents. These additives represent typically less than 5 % in weight of the solids present in aqueous dispersion finale. Par elsewhere by adapting the volumetric quantity of pigment and the final content of solid matters and additives in the formulas of coating, one can obtain different quality from finished painting going from the chechmate to very shining according to the final destination from painting. In more of the particular applications described in detail above, the aqueous compositions of coating according to the invention can be used to also carry out adhesives. adhesives sensitive to pressure (PSA), varnishes of overprinting and industrial compositions of painting. Industrial paintings of coating are applied and dried under perfectly defined and maitrized conditions. Most of the time the application of industrial painting is one of the stages of the manufacture of the painted objects. One can quote the application of painting or varnished by pulverization, soaked or rollers on wood, plastic or metal (gone of the car, the electric household appliances, furnishing and coil-coating etc...). When one implements them, dispersions according to the present invention, including the possible additives, are applied quite simply to a surface, their thickness lying between approximately 25 and approximately 100 driven m, using a brush, of a roller or any other average good known in the métier. Ensuite, one lets dispersion reticulate at temperatures ranging between approximately 5 Degree c and approximately 40 Degree c; preferably, in particular, between approximately 5 Degree c and approximately 25 Degree c and more particularly still between approximately 5 Degree c and approximately 15 DEG C In the 12 hours following the application, dispersion starts to reticulate and

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form a hardened film. At the end of 48 hours, the reticulation is finished to at least 85 %. One can renew the application to obtain multiple coats of paint. In more of the aesthetic properties and physics which they bring, the products of coating according to the invention contain much less volatile organic substances (SOV) that majority of paintings, if not all. that one finds it in the trade. They are products ideals for marketing. The examples which follow give a more detailed description of the invention. Except contrary indication, the parts and percentages indicated are in weight. The degree of reticulation of films is given in the examples by tests of search for their content of gel and by the calculation of their swelling number. These determinations are carried out on films given up in the environmental conditions during at least 48 hours. The films are withdrawn from the substrate and are tested as follows: (1) one weighs in bottles out of glass of the doubles of the samples of the films whose weight is about 2 G; (2) one adds 75 ml of toluene in each bottle which one seals and agitates vigorously; (3) at the end of three days, one deposits the contents of the bottles on a nylon sieve with fine meshs which one weighed and one washes à fond with toluene; (4) the sieve is weighed, then one makes dry vacuum in a drying oven and one weighs; (5) after having determined the weight of wet freezing and dry freezing, the content of gel and the swelling number are calculated as follows: Content of gel, % = weight of dry freezing X 100 DIVIDED weight of film Swelling number = weight of wet freezing - weight of dry freezing DIVIDED weight of dry freezing The contents of gel of at least approximately 95 % and the swelling numbers lower than 5 indicate than the reticulation of films was satisfactory.

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Pour obtenir des compositions formant des revêtements ayant des propriétés supérieures lorsqu'elles réticulent à la température ambiante ou à des températures élevées, il faut, dans les modes de réalisation préférentiels, que le glycidyl et l'acide

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In English:

Example 1 Into an engine suitable equipped with two bulbs with bromine, of a condenser, an agitator and a thermometer, one introduces 355 parts of water, 1,95 parts of sodium bicarbonate and 9,83 parts of surface-active, namely of nonyl phényl polyethylene glycol phosphatic ether. In one of the bulbs with bromine, one adds 11,45 parts of methyl methacrylate, 128,57 parts of acrylate of butyl, 10 parts of acétoacétoxyéthyl methacrylate, 7,5 parts of acrylic acid and 22,5 parts of glycidyl methacrylate. Into the second bulb with bromine one introduces 40,43 parts of water and 1,13 parts of ammonium peroxydisulfate. One starts to agitate and to heat until the temperature in the engine reaches 85 DEG C.On introduced into the engine an initial load of 0.06 part of ammonium peroxydisulfate in 19,5 parts of water and one starts to slowly add the monomers and catalyst. The temperature being maintained to 85 Degree c, one adds the monomers throughout one 2 hour and catalyst throughout one 5 minute and 2 hour. One lowers the temperature to 70 Degree c and one adds 0,3 part of t-butylhydroperoxyde. One lowers then the temperature to 35 Degree c and one adds a solution of 0,3 part of formaldehyde sulfoxylate of sodium in 9,89 parts of water. When the temperature reaches 25 Degree c, one adds 4,89 parts of ammonium hydroxide to 28 % and 1,18 parts of inhibitor of development of bacteria. The stable latex that one obtains has a viscosity of 25 mPa.s. a content of solids of 40,45 % and a pH of 5,2. One adjusts the pH of a part of latex with 7,5 with ammonia and then with 9,0 with sodium hydroxide (e.g. 1A). One adjusts of it another part with 9.0 with hydroxide of tétraméthylammonium (e.g. 1B). One deposits films on plates glass and one subjects them to the environmental conditions during 48 hours. One detaches films of the substrate and one subjects them to the tests whose results appear in Table 2. Example 2 One proceeds as described in example 1 and one polymerizes 143.76 parts of methyl methacrylate, 165,79 parts of acrylate of butyl, 9,03

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parts of methacrylic acid, 14,45 parts of acétoacétoxyéthyl methacrylate and 28,9 parts of glycidyl methacrylate. The latex obtained has a viscosity of 1 100 mPa.s and a content of solids of 47,32 %. One adjusts the pH of latex with hydroxide of tétraméthyl ammonium. One deposits films on glass plates which one subjects to the environmental conditions during 48 hours. The film resists 108 frictions in to and from with méthyléthylcétone. The results of the tests carried out with other films appear in Table 2. Example 3 One proceeds as described in example 1 and one polymerizes 111,49 parts of methyl methacrylate, 128,57 parts of acrylate of butyl, 5,01 parts of acrylic acid, 7,42 parts of acétoacétoxyéthyl methacrylate and 10,2 parts of glycidyl methacrylate. The latex obtained has a viscosity of 27,5 mPa.s, a content of solids of 40,74 % and a pH of 7,45. The pH is adjusted to 7.5 with ammonia and 9,0 with sodium hydroxide. The films carried out starting from this latex are tested after being subjected to the environmental conditions during 48 hours. The results of the tests appear in Table 2. Example 4 One proceeds as described in example 1 and one prepares a latex by polymerizing 111,49 parts of methyl methacrylate, 128,57 parts of acrylate of butyl, 5,02 parts of acrylic acid and 22,06 parts of acétoacétoxyéthyl methacrylate. The latex has a viscosity of 22,5 mPa.s, a content of solids of 39,88 % and a pH of 7,38. One adjusts the pH with 7,5 with ammonia and 9,0 with sodium hydroxide. The films carried out starting from this latex are tested after being subjected to the environmental conditions during 48 hours. The results appear in Table 2. Example 5 One proceeds as described in example 1 and one prepares a latex by polymerizing 142,13 parts of methyl methacrylate, 163,87 parts of acrylate of butyl, 6,4 parts of acrylic acid and 19 parts of glycidyl methacrylate. The latex has a viscosity of 147,5 mPa.s, a content of solids of 45,74 % and a pH of 7,4. One adjusts the pH with 9,0 with ammonia and hydroxide of sodium. The films carried out starting from this latex are tested after being subjected to the environmental conditions during 48 hours. The results of the tests appear in Table 2. Example 6 One proceeds as described in example 1 and one prepares a latex by implementing 145,8 parts of methyl methacrylate, 168,1 parts of acrylate of butyl and 9,83 parts of acrylic acid. The latex has a viscosity of 1 650 mPa.s, a content of solids of 45,34 % and a pH of 7,3. One adjusts a part of latex with

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7,3 with ammonia. One adjusts the pH of another part of latex with 9,0 with hydroxide of tétraméthylammonium (TMAH). The films carried out starting from this latex are tested after being subjected during 48 hours to the environmental conditions. The film carried out with the part containing of the TMAH resists 38 frictions in to and from with méthyléthyl-ketone. The results of the tests appear in Table 2. Example 7 One proceeds as described in example 1 and one prepares a latex by polymerizing 153,11 parts of methyl methacrylate, 176,47 parts of acétoacétoxyéthyl methacrylate and 21,73 parts of glycidyl methacrylate. The latex has a viscosity of 75 mPa.s and a content of solids of 39,88 %. One adjusts the pH with 9,0 with TMAH. The films obtained starting from this latex are tested after being subjected during 48 hours to the environmental conditions. The results of the tests appear in Table 2. Example 8 One proceeds as described in example 1 and one prepares a latex by polymerizing 120 parts of methyl methacrylate, 138,74 parts of acrylate of butyl and 8 parts of acrylic acid. The latex has a viscosity of 20 mPa.s and a content of solids of 40,38 %. One adjusts the pH with 8,5 with TMAH. The films obtained starting from this latex are tested after being subjected during 48 hours to the environmental conditions. Example 9 One proceeds as described in example 1 and one prepares a latex by polymerizing 39,04 parts of methyl methacrylate, 110,84 parts of methyl methacrylate 18,35 parts of methacrylic acid, 45,85 parts of acétoacétoxyéthyl methacrylate and 91,76 parts of glycidyl methacrylate. The latex obtained has a viscosity of 15 mPa.s and a content of solids of 40,96 %. One adjusts the pH with 8,5 with TMAH. The films obtained starting from this latex are tested after being subjected during 48 hours to the environmental conditions. The results of the tests appear in Table 2. EMI16.1 EMI17.1 The coatings prepared starting from the compositions according to the present invention are those of examples 1, 2, 3 and 9. Example 10 Into an engine equipped with a condenser, of an agitator, a thermometer and two proportioning pumps one introduces 431 parts of water, 10,28 parts of surface-active, namely of nonylphénylpolyéthylèneglycol phosphatic, and 1,98 parts of sodium bicarbonate. One starts to agitate and one heats until the temperature reaches 75 DEG C One adds an initial load of 0,07 part of ammonium persulphate. While maintaining the temperature with 75 Degree c, one pumps in the engine throughout

one 2 hour and 30 minutes a mixture of monomers made up of 1,97 parts of ethyleneglycol diméthacrylate, 24,99 parts of acétoacétoxyéthyl methacrylate, 49,57 parts of glycidylméthacrylate, 50,92 parts of styrene and 66,99 parts of acrylate of butyle Simultanément, one pumps in the engine throughout one 45 minute and 2 hour a solution of initiator made up of 0,59 parts of persulphate of ammonium and 21,12 parts of water. 45 minutes after having finished the addition of the aforementioned solution of initiator, one starts to add throughout also 45 minute and 2 hour one second load of solution of initiator made up of 0,59 parts of persulphate of ammonium and 21,15 parts of water. At the same time as this second addition of monomer, one pumps in the engine throughout one 2 hour and 20 minutes a second mixture of monomers made up of 4,13 parts of acrylic acid, 1,88 parts of methacrylic acid, 59,44 parts of methyl methacrylate and 129, 74 parts of acrylate éthyle Après to have added all the mixtures of initiators and monomers, one maintains the temperature with to 75 Degree c continuously to agitate during 45 minutes. One lowers the temperature to 70 Degree c and one adds 0,5 part of hydroperxoxyde from t-butyl(actif à 70.%). After having cooled to 35 Degree c, one adds a solution made up of 0,5 parts of métabisulfite of sodium and 10 parts of water. One adjusts the pH of latex with 8,5 with TMAH to 10 %. the content of gel of latex is 96,0, the swelling number of 3,3, the tensile strength of 13789 X 10 Pa, the lengthening of 180 %, the viscosity of 100 mPa.s, the content of solids of 43 % and the minimal temperature of formation of film of 10 Degree c. Example 11 11-1: preparation of latex Into engines equipped with a condenser, of an agitator, a thermometer and means of food, one introduces 1450 parts of deionized water, and 42,4 parts of surface-active which an ether of nonylphenylpolyethylene glycol phosphatè. Agitation is begun and, after setting in complete solution of surface-active, one adjusts the pH with 3,8 by addtion of a solution of sodium hydroxide with 10%. One heats the engine until reaching a temperature of 80 DEG C One introduces into the engine an initial load of 0,32 parts of ammonium peroxydisulfate in 5 parts of water, follow-up immediately of the addition during 2 hours and 30 mn of a mixture of monomers including/understanding 203,2 bet glycidylméthacrylate, 208,8 parts of styrene, 275,2 parts of acrylate of butyl, 8,0 parts of éthylénéglycol

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diméthacrylate and 102,4 parts of acétoacétoxyéthyl méthacrylate.En even time one carries out 2 additional food comprising 2,4 parts of an igniter peroxydisulfate of ammonium dissolved in 87,5 parts of water and a formed plug of 5,6 parts of sodium bicarbonate dissolved in 87 parts of water. One introduces this 2 food supplèmentaires during 2 hours 40 minutes by maintaining the mixture reactional with 80 Degree c. The food terminèes, one lowers the temperature of the reactional medium to 750 Degree c during one hour. With the end of this hour, one introduces 8,0 parts of methacrylic acid, 17,0 parts of acrylic acid, 244 parts of methacrylate deméthyle and 532,8 parts of ethyl acrylate. This introduction lasts 2 hours and 30 minutes. In way concomittente, one introduces an initiator and a plug during 2 hours 40 minutes by maintaining the temperature to 75 DEG C.On cools resulting latex and one adds to latex a solution of 2,1 parts of hydroperoxide of T-butyl. To 35 Degree c one adds to latex during 15 minutes a solution of 2,1 parts of sodium pyrosulphite dissolved in 40,0 parts of water. Latex obtained is still cooled and it is discharged. It has a pH of 5,9 a viscosity of 62 mPa.s and a content of solids of 46,8 %. a part of this latex is preserved of the state and is called latex A, the other part is ajustè with pH 8,5 by a solution to 10,5 % of ammonium hydroxide and is appelè latex B One calls latex A, the latex obtained with pH = 5,9 on the outlet side of the engine and latex B, the latex with pH 8,5 mentralized with ammonia. 11-2: Characterization of latexes The films delatex are formed and conditioned to 22 Degree c and 50% of relative humidity. 1. Measurements of swelling: The degree of reticulation of films resulting from dispersions of Ambicure is determined by measurement of swelling in trichorethylene. (1) the latex film is cut out of pieces of approximately 0,25 G (2) the sample is weighed with precision then placed in a mesh basket of 112 driven m (3) the basket containing the sample is then immersed in trichlorethylene. (4) After 24h, the sample is weighed and the percentage of swelling of film of given Ambicure. The calculation of % of swelling is carried out according to the following formula: % Gon = (Mgon - Mfilm)*100/Mfilm where Mgon, represents the weight of it sample inflated by solvent and Mfilm, the weight of the sample before immersion. % of swelling obtained respectively after 1 and 7 days are indicated below: Columns=3 Head Collar 1: Latex Head Collar 2: % Head Collar 3: %

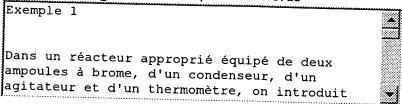
SubHead Collar 1: SubHead Collar 2: Swelling (24h) SubHead Collar 3: Swelling (7 J) A 874 661 B 603 514 2 Measurements of allongement/rupture: The results in term of allongement/rupture, arpès 7 days of maturation of films, are indicated below: Columns=3 Head Collar 1: Latex Head Collar 2: Lengthening % Head Collar 3: Stress the rupture (MPa) Latex A 195 6,7 Latexes B 225 8,3 Persoz hardness is given after 7 Days of maturation of films. It is 73 for latex A and 87 for the latex B. Example 12 With an engine equipped with a condenser, of an agitator, a termometer and means of food, one adds 400 parts of deionized water and 10,32 parts of surface-active to knowing an ether of monylphenylpolyethylene glycol phosphatè. One starts to agitate and once termine the addition of surface-active, one regulates the pH by addition of 1,98 parts of sodium hydrogénocarbonate. One increases the temperature inside the engine to 75 DEG C One carries out a first load of 0,07 part of ammonium peroxydisulfate in 5 parts of water, followed immediately by the addition during 2 hours 30 minutes of a mixture of monomers comprising 74,91 parts of styrene, 17,35 parts of acrylate of butyl, 1,92 parts of éthyléne glycol methacrylate 37,35 parts of acétoacétoxy éthylméthacrylate and 1,84 parts of acrylate of éthyle On load at the same time 0,59 parts of ammonium péroxydisulfate dissolved in 21,1 parts of water. This derniére load is effectuée during 2 hours and 40 minutes by maintaining the mixture reactional to 75 DEG C These loads terminées, one maintains the temperature of the reactional mixture with 75 Degree c during 1 hour. At the end of one hour one begins a load comprising 2,2 parts of methacrylic acid, 3,91 parts of acrylic acid, 57,49 parts of acrylate of butyl and 126,53 parts of styrene. One introduces these monomers during 2 hours and 30 minutes. At the same time one introduces the same solution of initiator as above during 2 hours and 40 minutes by maintaining the temperature to 75 DEG C One cools latex obtained with 70 Degree c and one adds to latex a solution including/understanding 0,5 parts of a solution with 70 Degree c of hydroperoxide of tbutyle. On adds to 35 Degree c with latex a solution of 0,5 parts of sodium pyrosulphite dissolved in 10,0 parts of water. Latex obtained is still cooled and one discharges it from the engine. It has a pH of 5,4 then, a viscositè of 30 mPa.s and a content of solids of 44,0 %. the pH of latex is regulated to 8,5 per

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addition of a solution of ammonium hydroxide with 10%.

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In English:

Example 13 With an engine equipped with a condenser, of an agitator, a thermometer and means of food, one adds 800 parts of deionized water and 20,72 parts of surface-active to knowing an ether of monylphenylpolygethylene glycol phosphatè. One starts to agitate and once terminèe the addition of surface-active, one régle the pH by addition of 3,96 parts of sodium hydrogénocarbonate. One increases the temperature inside the engine to 75 DEG C One carries out a first load of 0,14 part of ammonium peroxydisulfate in 5 parts of water, followed immediately by the addition during 2 hours 30 minutes of a mixture of monomers comprising 104.0 parts of glycidyl méthacrylae, 32,0 parts of styrene, 179,0 parts of acrylate of butyl, 4,04 parts of éthyléne glycol methacrylate and 54,40 parts of acétoacétoxyéthyléméthacrylate. On load at the same time 1,18 parts of ammonium peroxydisulfate dissolved in 42,3 parts of water. This dernière load is carried out during 2 hours and 40 minutes by maintaining the mixture reactional to 75 DEG C These loads finished, one maintains the temperature of the reactional mixture with 75 Degree c during 1 hour. At the end of one hour one begins a load comprising 4,07 parts of methacrylic acid, 7,96 parts of acrylic acid 71,67 parts of methyl methacrylate and 336,3 parts of ethyl acrylate. One introduces these monoméres during 2 hours and 30 minutes. At the same time one introduces the same solution of initiator as above during 2 hours and 40 minutes by maintaining the temperature to 75 DEG C One cools lelatex obtained with 70 Degree c and one adds to latex a solutionà 70% of hydroperoxide of t-butyle.On adds to 35 Degree c to latex a solution of 1.0 parts of sodium pyrosulphite dissolved in 20,0 parts of water. Latex obtained is still cooled and one discharges it from the reagor. He then has a pH of 8,1, a viscosity of 140 mPa.s and a content of solids of 46,8%. The pH of latex is regulated to 8,5 per addition of a solution of ammonium hydroxide with 10%. Example 14 A) Formulation of coating for wood One prepares

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a formulation of transparent coating for wood by dispersing 667 parts of the composition according to example 10, 1 part of a dioctyl sulfosuccinate of sodium in a medium made up of 169,6 parts of water, 4 parts of Rheolate 300, thickener marketed by Rheox Inc, 2,2 parts of Colloid 652, antifoaming, marketed by Rhône-Poulenc Inc, 25,9 parts of propylèneglycol being used as modifying agent and 5.7 parts of ammonium hydroxide. This formulation has a content of COV (organic compounds volatile) of 34.0 a/l. Its content of solids is 35.3 % in weight or 32.5 % in volume. The viscosity of Stormer of this formulation is of 61 +/- 3 KU. One compares the present formulation with two products which one finds in the trade and which are sold like products of coating for wood. One measures the following properties at the same time formulation according to the invention and of the products commercial: 1) Content of COV expressed in grams per liter 2) Percentage in weight of subsances not birds 3) the brilliance to 60 DEG and 20 DEG is measured by forming a film of 75 driven m using a car-film on a chart Leneta Form 2C 4) the hardness of the pencil is measured using test ASTM D-3363 5) resistance to the gel/dégel is measured using test ASTM 2243 6) the duration of drying is measured as from the moment when the composition is applied until it is dry with the touch when it is applied with drawing to an apparatus Leneta Form 2 C Card to 22 Degree c and to 60 DEG and 20 DEG on wood of poplar - the formulations of coating for wood are applied using a nylon brush to wood of poplar and are dried. One repeats this operation at two hours of interval until application of three complete layers. 8) resistance to the prints is given while placing during ten minutes a coffee cup out of porcelain containing 175 G of water with 79 Degree c on a surface revêtue. On withdraws the cup and one proceeds to a qualitative evalutation of resistance to the prints. 10 corresponds to an excellent resistance to the prints. 9) Resistance to the products chimiques/solvants: the resistance of the composition of coating to various solvents and domestic chemicals is measured as follows: one applies three (3) drops of each solvent to the coating, one covers solvent with a watch glass during four (4) hours, one withdraws the watch glass and the product tested and one carries out the qualitative analysis of the test-tube on a scale going from 0 to 10, 10 being best the résultat. On uses following solvents and domestic products and one adds the

results with each product to obtain the value indicated in Table 4: water, vodka, cleaning Fantastik TM, dissolving for nail varnish, dissolving for nail varnish without acetone, coffee, tea, juice of lemon, ketchup, mustard, hydroxide of sodium to 10 % and red wine. The results of the tests above appear in Table 3. Id=Tableau 3 Columns=4 Head Collar 1: Head Collar 2: Formulation Head Collar 3: Product Head Collar 4: Product SubHead Collar 1: SubHead Collar 2: according to invention SubHead Collar 3: commercial A SubHead Collar 4: commercial B Content of COV (g/l) 34,0 Not-birds 35,4 34,0 32,0 Brilliance, 60 DEG /20 DEG 3 millet 86/82 89/54 94/66 Hardness pencil 6B 2B 4B Resistance gel/dégel (undergone cycles) 5 5 5 Times drying (complete, mn) 3,5 (SEP) 10 5,0 Brilliance, 60 DEG /20 DEG, poplar, with grain 3 layers 66/15 58/10 66/14 Resistance to the prints (10=très well, bad 0=très) 10 9 10 Maximum Prod.chimigues/solvants Resistance = 120 92 82 92 The results above show that the formulation according to the invention containing latex of example 10 makes it possible to obtain comparable performances, even higher than those of the two products commercial. The formulation according to the invention has, on the other hand, a very weak content of COV and, consequently, present with regard to the environmental protection a greater interest than the two products commercial. Example 15 B) Formulation of gloss paint: One prepares a formulation of ultra-brilliant white painting by dispersing 580,0 parts of the composition according to example 10, 2,0 parts of dioctyl sulfosuccinate of sodium (Pentax 99, marketed by Rhône-Poulenc Inc), 14,0 parts of Rheolate 300, thickener marketed by Rheox, Inc. 4,0 parts of ammonium hydroxide. 12,0 parts of an agent of coalescence, namely of tripropylèneglycol méthyléther (Dawanol TPM, marketed by Dow Chemical Company) and 4,0 parts of Foamex 1488 (antifoaming, marketed by Tego Chemie Service the USA) in a medium made up of 170,0 parts of water, 9,0 parts of Colloid 111, agent of anion dispersion, marketed by Rhône-Poulenc Inc. surface-active nonionic, namely a alkylphénoxy-poly (éthylèneoxy) modified ethanol, marketed by Rhône-Poulenc Inc, 1,0 part of 2-amino-2-methyl-1-propanol containing 5 % of water (AMP, marketed by Angus Chemicals, Northbrook, IT), 25,9 parts of propylèneglycol, 2,0 parts of Foamex 1488 and 180,0 parts of Ti-Pure R700, pigment containing rutile, sold

by E.I. Dupont. This formulation of painting has a density of 1,2 kg/l and a content of COV (organic compounds volatile) lower than 50,0 g/l. The content of solids of the formulation is 45,4 % in weight or 34,6 % in volume, the pigmentary concentration in volume (PVC) of 15,2, the pH of 8,9, the viscosity of Stormer of 100 KU +/- 2 and viscosity HERE "Cone & Plate" of 0,70 P +/- 0.05. One measures the following characteristics of this formulation according to the invention: 1) the brilliance to 60 DEG and 20 DEG is measured using test ASTM D-523. The values obtained for the brilliance under the angles of measurement are respectively 86 and 61, 2) resistance to the run-out is measured using test ASTM D-4400. The value measured of 250 is driven m. 3) levelling is measured using test ASTM D-4062. the best result being noted 9. The value obtained for the formulation according to the invention is 9, 4) wet adhesion on painting brilliant alkyde is measured using test ASTM D-3359. Adherence is excellent. The measured value is 10. The data above show that the film obtained with the formulation of painting according to the invention, containing latex obtained in example 10, presents a brilliance, a resistance to the blocking (to be able anti-blocking), an adhesion in a wet state and other properties which all, are excellent. Compared to the other products which one finds in the trade for similar applications, the formulations according to the invention present performances equal or higher than those of the aforesaid marketed products. Moreover, the content of COV of the formulation according to the invention is lower than 50 g/l, which constitutes a result definitely higher than that of the formulations of the trade whose content of COV is generally located between approximately 350 and approximately 380 g/l. The principles, the preferential mode of realization and the operating modes of this invention were described above. However, the present invention which is intended to be protected should not be interpreted as limited to the described particular forms since these last must be regarded an illustration of the invention and not as a restriction of this one. The specialist of the profession can bring variations and changes without deviating from the spirit of the invention. Example 16 Formulation in flat One obtains a formulation of matt white painting by dispersing 1500 parts of the composition according to example 13, 40 parts of Tylose MH 6000 XP. cellulose thickener marketed by Hoechst, 37 parts of

Coatex P 50, dsipersant polyacrylic marketed by Coatex, 20 parts of Bevaloid 6681, antifoaming marketed by Bevaloid, 9 parts of Proxel data base, biocide marketed by Zénéca, 530 parts of RL 68, titanium dioxide marketed by Thann and Mulhouse, 2130 parts of Omyalite 90 and 3200 parts of Durcal 5, calcium carbonates marketed by Omya and 3090 parts of water. This formula of painting has a pH (ajustè by a soda solution with 30%) of 8,5 a pigmentary concentration in volume of 75 %, a mass dry extract of 63,4 % and a viscosity Brookfield RVT measured with 50tr:min with 23 Degree c using pin 5 of 3480 mPa.s. The abrasion resistance wet of this formulation according to the invention was carried out according to DIN standard 53778 and made it possible to obtain 7200 cycles, which is particularly remarkable for a formula not containing a solvent. Example 17 Formulation in satin-finish paint One obtains a formulation of white painting glossed by dispersing 428 parts of the composition according to example 13, 15 parts of Rhéo 2100, associative thickener marketed by Coatex, 5 parts of Coatex Br 3, polyacrylic dispersant marketed by Coatex, 3 parts of Bevaloid 6002, antifoaming marketed by Bevaloid, 2 parts of Proxel GXL, biocide marketed by Zénéca, 195 parts of RL 68, titanium dioxide commercialisè by Thann & Mulhouse, 146 parts of Hydrocarb 90, calcium carbonate marketed by Omya and 202 parts of water. This formula of painting has a pH (adjusted by 5 parts of a soda solution of 30%) of 9, a pigmentary concentration in volume of 33 %, a mass dry extract of 56,9 % and a viscosity Brookfield RVT measured to 50 tr/min with 23 Degree c using pin 5 of 7680 mPa.s, with a content of COV lower than 50 g/l. Various characteristics were measured on this formulation according to the invention: 1) the brilliance to 60 DEG after application to 300 driven m wet on glass plate and drying to 23 Degree c and 55 % of relative humidity during 24h was measured to 16. 2) resistance to the blocking, evaluated according to a test consisting in applying painting to a PVC sheet (standard Lénétal), drying during 48h to 23 Degree c and 55% of humiditè relative, placing 2 strips face painted against face painted with a weight of 500g on a surface of 4 cm and evaluating the force necessary to separation on a scale of 0 if the strips remain stuck to 10 when separation is immediate, was placed to 10. This performance is thus completely interesting for a painting atvery weak rate of COV, the traditional products being at too soft

polymer base either to reach this comportement, or containing products hard but plasticized using solvents.

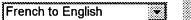
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Exemple 13

A un réacteur équipé d'un condensateur, d'un agitateur, d'un thermomètre et de moyens d'alimentation, on ajoute 800 parties d'eau

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Example 18 Formulation in gloss paint One obtains a formulation of brilliant white painting by dispersing 570 parts of the composition according to example 11, 29 parts of Acrysol RM 2020, associative thickener marketed by Rohm & Haas, 3 parts of Bevaloid 6770, disperssant polyacrylic commmercialisè by Bevaloid, 1,6 parts of Tegofoamex 1488, antifoaming marketed by Golsdschmidt, 177 parts of RHD 2, dioxide of titanium marketed by Tioxyde, 1 part of - amino 2methyl 1-propanol in solution to 90 % (AMP 90) commercialisè by Angus, 3 parts of Dowanol DPnB, agent of coalescence marketed by Dow and 220 parts of eau. Cette formula of painting has a density of 1.2 kg/dm a pH (e Tegofoamex 1488, antimousse commercialisé par Golsdschmidt, 177 parties de RHD 2, dioxyde de titane commercialisé par Tioxyde, 1 partie de - amino 2-méthyl 1-propanol en solution à 90 % (AMP 90) commercialisè par Angus, 3 parties de Dowanol DPnB, agent de coalescence commercialisé par Dow et 220 parties d'eau. Cette formule de peinture présente une masse volumique de 1,2 kg/dm un pH (ajusté par 6 parts of an ammonia solution with 20%) of 9, a pigmentary concentration in volume of 16 %, a mass dry extract of 46% and one viscosity Brookfield RVT measured to 50 tr/min with 23 Degree c using pin 5 of 1200 mPa.s, with a content of COV lower than 50g/l. Various characteristics were measured on this formulation according to the invention: 1) the brilliance to 20 DEG after application with 300 driven m wet on glass plate and drying to 23 Degree c and 55 % of humidity relative during 24h to measured summer with 64. 2) resistance to the blocking. evaluated according to a test consisting in applying painting to a PVC sheet (standard Lénétal), drying during 48h to 23 Degree c and 55% of relative humidity, placing 2 strips face painted against face painted with a weight of 500g on a surface of 4 cm and evaluating the force necessary to separation on a scale of 0 if the strips remain stuck to 10 when

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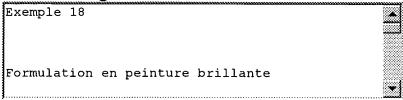
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separation is immediate, was placed to 10. 3) the evaluation of tended by the notched gauge Erichsen led to a value of 0,5 mm. 4) the evaluation of the runouts using the notched gauge Erichsen gave a measurement of 200 driven m. In addition, the wet test of adhesion on old funds alkyls appeared excellent. These performances correspond to a level at least equivalent to aqueous commercial paintings. but to a level of COV very appreciably lower. Example 19 Formulation in industrial painting It acts of a white painting intended for industry in general. this painting can be applied by pulverization to metal parts into full-course or completion. One obtains this formulation of industrial painting by dispersing 580 parts of the composition according to example 12, 29,6 parts of Acrysol RM 2020, associative thickener marketed by Rohm & Haas, 3 parts of Bevaloid 6770, dispersant polyacrylic commercialisè by Bevaloid, 1,6 parts of Tegofoamex 1488, antifoaming marketed by Goldschmidt, 180 parts of RHD 2, dioxide of titanium marketed by Tioxyde, 1 part of 2-amino 2-methyl 1propanol in solution to 90 % (AMP 90) marketed by Angus, 29 parts of Texanol, agent of coalescence marketed by Eastman Chemical, 5 parts of Inhibition 92, agent anti-flash rust marketed by Bourigeaud, 1 part of Triton GR7M, marketed by Union Carbide. and 214 parts of water. This formula depeinture has a density of 1,2 kg/dm a pH (adjusted by 6 parts of an ammonia solution with 20%) of 9, a pigmentary concentration in volume of 16%, a mass dry extract of 43 % and a content of COV lower than 50 g/l. The evaluation of different carateristic from this formulation according to the invention was carried out in the following way: Painting was applied to degreased steel LAF plates thickness 0,8 mm with a threaded rod of 100 mm wet in order to obtain a dry thickness of 25 mm. The plates thus covered are dried 30 minutes with 60 Degree c then conditioned 48h with 21 Degree c and 60% of relative humidity. 1) chemical resistance to solvents was evaluated according to a test consisting in rubbing the plate covered with ombidé a solvent cotton plug. A weight of 500 G is applied to the plug and one evaluated the state of film after 100 comings and goings of the plug (at a speed of 62 comings and goings per minute). The test was carried out with like solvent the ethanol and the Methyl Ethyl Cétone. In both cases after 100 comings and goings, the support, does not appear and the film does not seem not degraded. 2) the impact resistance of this painting was evaluated by

fall of mass according to method NF T 30-039. Painting according to the invention made it possible to obtain an impact resistance higher than 100 cm with a mass of 1 kg, which translates a remarkable flexibility of film. These performances corresponding to a level are equivalent to solvantées commercial paintings, but to unniveau of COV very appreciably lower. In addition from excellent results (for the tests described above) were also obtained by drying films of painting according to the invention at temperatures lower or higher than 60 Degree c.

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